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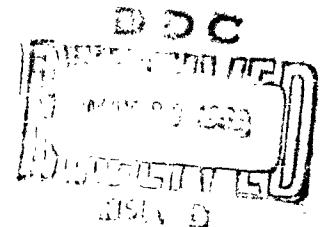
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**RESPONSE OF CHARRING ABLATORS  
TO HYPERTHERMAL ENVIRONMENT**

R.D. MATHIEU



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**SPACE SCIENCES LABORATORY**

**GENERAL  ELECTRIC**

**MISSILE AND SPACE DIVISION**

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# SPACE SCIENCES LABORATORY

## AEROPHYSICS SECTION

(6) RESPONSE OF CHARRING ABLATORS TO  
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by

R. D. Mathieu\*\*

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\*\* Research Engineer, Gas Dynamics

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# ABSTRACT

A study is made of the thermal response of charring ablators to given environmental conditions. The heat protective materials considered form gases and a porous char as they undergo thermal degradation in depth. The analysis considers the transient conditions and the effect of the surface pressure on the gas pressure build-up within the porous char. The effects of porosity and permeability are included.

Results of the temperature, material density, and gas pressure distribution through the heat protective layer are presented for a typical charring material. Two cases are considered: in the first case, the material undergoes one degradation reaction; in the second case, the material undergoes two successive reactions.

The inclusion of char removal can also be accomplished by this study.

↑

## A. INTRODUCTION

The purpose of this investigation is to determine the thermal response of a charring ablator when subjected to given environmental conditions, such as those for a typical re-entry trajectory. In particular, the transient effects as well as the pressure effects due to the formation of gases within the material are included.

Charring ablators are finding applications in re-entry ballistic missiles, manned entry vehicles, and rocket systems because of their efficient ablation performance (Ref. 3). Such material systems provide a relatively simple means for providing thermal protection over a wide range of environmental conditions. As a result, charring plastics have received considerable attention (Refs. 1, 2).

When these materials are subjected to re-entry environmental conditions, they undergo pyrolysis during which gases and a porous carbonaceous char are formed. The char is then removed by an erosion process, such as surface oxidation, vaporization, or spallation.

It is interesting to look at the degradation process for a typical high performance castable ablation resin (Ref. 14), which degrades in essentially three temperature dependent steps:

- (1) The first step is a mild pyrolysis during which a very small percentage of gases are given off. The temperature range is approximately  $100^{\circ}\text{C}$  to  $270^{\circ}\text{C}$ .
- (2) The second step is a much more violent pyrolysis during which approximately 50% of the weight of the plastic decomposes into heavy molecular weight gases. The remaining plastic is a foam-like organic porous char. The temperature range is approximately  $290^{\circ}\text{C}$  to  $340^{\circ}\text{C}$ .
- (3) The third step is a decomposition of the primary char into a hard, carbonaceous secondary char. At the same time, a small quantity of low molecular weight gases are evolved. This decomposition proceeds until practically all of the primary char has been transformed. The temperature range is approximately  $400^{\circ}\text{C}$  to  $700^{\circ}\text{C}$ .

An additional feature is mechanical spallation. It appears that the primary char grows to a certain thickness, then slows down until the secondary char forms and grows to essentially the same thickness. At this point, there is a sudden increase in pressure due to the rapid evolution of large quantities of gas associated with the formation of a new primary char. This causes the char layer to pop off. It is very likely that the failure occurs immediately below the secondary char layer where the material is still in a plastic state. If this is the case, the thermal stresses will not play an important role in the spallation phenomena. Very little is known about the failure stresses of char forming materials, therefore, it is difficult to predict the removal of char material due to spallation.

For such materials, it is evident that the transient conditions and gas pressure are important because of the periodic spallation. The transient effects are also important when the environmental conditions are changing rapidly, or the heat fluxes are small enough such that it takes a relatively long time for steady-state conditions to be reached. In the same manner, the surface pressure is important since it controls the flow of gases through the porous char surface. The pressure also helps to determine the chemical reactions which can and do occur at the surface. The role of the pressure environment in the performance of charring ablators has been mentioned before (Refs. 9, 11, 12, 13).

The charring ablators are efficient as thermal protective materials because they possess several useful mechanisms for dissipating the heat and keeping the temperature in the material from reaching intolerable levels:

- (1) Heat is absorbed by the latent heat of decomposition of the material.
- (2) Gases flowing through the hot char absorb heat and tend to cool the char.
- (3) The cracking of the gases into lower molecular weight gases generally absorbs heat.

- (4) The large amount of gases entering the outer flow at the char surface reduces the heat flux because of the mass addition effect.
- (5) Such chars reach relatively high surface temperatures and are capable of re-radiating much of the heat.

The overall response of these materials to a given hyperthermal environment is quite complicated. A knowledge of the chemical kinetics for the decomposition of the original material, of the gases flowing through the porous char, and of the decomposition gases as well as the char surface interacting with the external flow is necessary. A knowledge of the physical properties of the original material, of the gaseous products, and of the char material is also necessary.

Numerous theoretical investigations of char forming plastics which undergo thermal degradation in depth have been conducted (Refs. 4 - 10). Transient conditions are considered in References 8 and 10, but the effects of the surface and internal gas pressure are neglected. Reference 9 considers the gas pressure drop through the char layer for quasi-steady state conditions.

The present analysis considers the coupled temperature-pressure effects on the transient ablation characteristics of a charring plastic. Thus, the effects of the internal structure of the degraded plastic material are included. Such an analysis should result in a better understanding and prediction of the ablation performance of these materials.

## **B. DESCRIPTION OF PHYSICAL MODEL**

The present analysis considers the transient thermal response of materials which decompose into gases and a porous carbonaceous char when exposed to a hypersonic environment. Thus, the basic system to be analyzed is one in which the plastic material changes to a porous char with gases flowing through it.

The degradation reaction or reactions occur over a range of temperatures. This permits the thermal protection system to be treated as a "continuous" system since the thermodynamic and mechanical properties of the material and gases change in a continuous manner through the material. The final char material, reaction zone, and original plastic material are treated as one continuous layer. It is not necessary to specify a definite degradation temperature (Ref. 10) nor define a reaction zone thickness (Ref. 9).

This formulation permits a detailed description of the flow of the gaseous products through the porous char. Since the gas flow is taken into account, it is necessary to make use of the equations for the conservation of mass and momentum of the gases in addition to the conservation of energy for the gas-char combination. It is assumed that the gas velocity is proportional to the pressure gradient and that the gases obey the equation of state for a perfect gas. The molecular weight of the gases is variable and taken to be a function of temperature since the cooler gases flowing through the hot char are heated and undergo thermal cracking. It is also assumed that the gases do not react chemically with the char or with themselves. The porous chars are generally quite homogeneous and the pore size sufficiently small such that there are many collisions between the gas particles and pore surface (Ref. 14). Therefore, it is assumed that the local gas and char temperatures reach the same value very rapidly (Ref. 4).

The heat flow and gas flow are normal to the surface, i.e., only the one-dimensional case is considered.

The basic analysis can be used to perform detailed calculations of the temperature, gas pressure, material density, and mass flux of gases through the material for a given re-entry trajectory. The ablation performance of a variety of materials which undergo thermal degradation in depth can be predicted. Additional phenomena which are characteristic of individual materials can be incorporated by modifying the boundary conditions (for the case of surface reactions) or performing additional calculations (such as thermal and mechanical stresses for spallation).

### C. BASIC EQUATIONS AND RELATIONS

Various forms of the basic conservation equations which govern the mass and heat flux through porous material have been presented and discussed in similar investigations (Refs. 9, 15 - 19). The basic equations can be obtained by considering a control volume of the porous medium fixed in space.

The porous material is assumed to be a homogeneous, isotropic material having an effective porosity  $f$ , i.e., the ratio of pore volume to bulk or total volume. This porosity is taken to be the same no matter how small of a volume is taken, i.e., the volume can not shrink to just solid material or to void space. Another quantity which arises is the ratio of the pore surface area to the total surface area. This quantity arises in determining the heat conducted in the gases, in the solid char material, and in defining an average gas velocity. This area ratio is taken to be equal to the porosity since the material is homogeneous and isotropic (Ref. 16).

#### Continuity Equation

The conservation of mass of the gases flowing through the porous char material is given by

$$\frac{\partial (f \rho_g)}{\partial t} + \frac{\partial (\rho_g u_g)}{\partial x} = \dot{w}_g \quad (1)$$

The velocity  $u_g$  is taken to be an average velocity, i.e., a mean velocity over an area large compared to the cross-sectional area of a single pore.

The term  $\dot{w}_g$  on the right hand side represents the rate of formation of gases per unit bulk volume of material. This is related to the chemical kinetics associated with the degradation process.

#### Momentum Equation

The momentum of the gas as it flows through the porous material is assumed to be given by

$$u_g = -K \frac{\partial P}{\partial x} \quad (2)$$

This is an empirical relation which states that the average velocity is linearly dependent upon the pressure gradient. The proportionality factor  $K$  is the permeability of the porous materials and is obtained from experimental results. It is a measure of the resistance of the material to the flow. Although the effective porosity is an indication of the permeability, it is not a measure of the permeability.

### Energy Equation

An energy equation for the overall conservation of energy within the material can be obtained by combining the energy equation for the gases with the energy equation for the solid material, or by considering the heat fluxes and possible heat absorption or generation mechanisms within a control volume of the bulk material (Ref. 18). The equation for the conservation of energy per unit bulk volume can be written as:

$$\begin{aligned}
 (\rho C_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_g u_g C_{p_g} \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} (k_{\text{eff}} \frac{\partial T}{\partial x}) + \dot{w}_p H_r \\
 - \rho_g u_g H_c \frac{\partial T}{\partial x} + u_g \frac{\partial p}{\partial x} + f \frac{\partial p}{\partial t}
 \end{aligned} \quad (3)$$

where

$$\begin{aligned}
 k_{\text{eff}} &= f k_g + (1-f) k_s \\
 (\rho C_p)_{\text{eff}} &= f \rho_g C_{p_g} + (1-f) \rho_s C_{p_s}
 \end{aligned}$$

The effective thermal conductivity for the bulk material including gas and solid is given by  $k_{\text{eff}}$ . This is equal to the thermal conductivity of the gas per unit bulk volume,  $f k_g$ , plus that of the solid material  $(1-f) k_s$ . The same thing is true for the effective heat capacity,  $(\rho C_p)_{\text{eff}}$ .

The respective terms in equation (3) represent:

- (1) Total heat stored in an element of porous material.
- (2) Net heat convected by the gas.
- (3) Net heat conducted through the porous material.
- (4) Heat absorbed due to the formation of the gases and char.

- (5) Heat absorbed due to the cracking of the gases.
- (6) The last two terms represent the work done on the gas by the pressure forces.

It should be mentioned that the term due to viscous dissipation is not included. The viscous effects are only present in the proportionality factor which appear in the momentum equation.

#### Equation of State

It is assumed that the gases present in the porous material behave as perfect gases. The thermodynamic properties are then related by the equation of state

$$p = \rho_g \frac{R}{\bar{M}} T \quad (4)$$

where  $\bar{M}$  is the mean molecular weight of the gases.

#### Rate of Degradation of Plastic Material

In general, the degradation of thermosetting plastic heat protective materials can be represented by an Arrhenius type of reaction or several reactions if the material degrades in successive steps (Refs. 6, 20). It is assumed that each of the individual reactions which occur during the degradation process follow the expression

$$\dot{w}_p = - A e^{-\frac{E}{RT}} \rho_{v.p.} \left( \frac{\rho_p - \rho_c}{\rho_{v.p.}} \right)^n \quad (5)$$

Here,  $\rho_c$  is the char density at which the individual reaction stops since the quantity  $(\rho_p - \rho_c)$  is a measure of the amount of material which is available for decomposition at any instant of time.

Care must be exercised in interpreting the experimental data which is necessary to determine the activation energy and frequency factor in equation (5). These are generally reduced from data obtained by TGA experiments for the particular material. In such experiments the rate of weight loss of very fine material particles is measured. These results must then be interpreted in terms of densities. In particular, the rate of gas formation is needed.

### Rate of Formation of Gases

The plastic material degrades into char and gases. The amount of gases given off per unit volume of material is not known exactly. Therefore, the rate of gas formation is obtained from the rate of degradation of the plastic material by defining a gasification ratio

$$\Gamma = - \frac{\dot{w}_g}{\dot{w}_p} \quad (6)$$

This represents the fractional part of the organic plastic material which enters the gas phase during the pyrolysis. The gasification ratio is generally treated as a constant.

The rate of gas formation as need in equation (1) is

$$\dot{w}_g = \Gamma A e^{-\frac{E}{RT}} \rho_{v.p.} \left( \frac{\rho_p - \rho_c}{\rho_{v.p.}} \right)^n \quad (7)$$

Each individual reaction which occurs during the overall pyrolysis can be written in a similar form.

### Porosity

The porosity of a porous material is defined as the ratio of pore volume to bulk volume of the char material. Initially, before the virgin plastic material is heated and degrades, the porosity is essentially zero. It finally becomes the value of the porosity for the char material,  $f_c$ , which is measured experimentally. The porosity is assumed to vary continuously during the degradation process. Therefore, it is written as a function of the instantaneous density of the plastic material

$$f = f_c \left( \frac{\rho_p - \rho_{v.p.}}{\rho_c - \rho_{v.p.}} \right)^a \quad (8)$$

Limited experimental results for glass-phenolic (Ref. 21) indicate that the value of  $a$  is approximately .75. It should be noted that these results were obtained for subsonic hyperthermal environments.

### Permeability

The permeability, which is the proportionality constant in equation (2), is a measure of the material resistance to the flow. It is also taken to be a function of the instantaneous density

$$K = K_c \left( \frac{\rho_p - \rho_{v.p.}}{\rho_c - \rho_{v.p.}} \right)^b \quad (9)$$

where  $K_c$  is the value of the permeability of the final char and is measured experimentally.

Equation (9) is a simplified expression. Actually, the permeability is a complicated function of pressure, temperature, viscosity of gases, pore size, and pore structure.

### Additional Quantities

In order to solve the previous set of equations (1) through (9), it is necessary to specify quantities such as the specific heat, thermal conductivity, heat of cracking, and molecular weight of the gases. In the present analysis, these quantities are taken to be functions of temperature. Experimental results are used to establish upper and lower limits for many of these quantities. The values used in the numerical example are tabulated as a function of temperature in Tables I and II.

### Boundary Conditions

Equations (1) through (4) can be combined into two partial differential equations for the pressure and temperature. These equations were solved by a numerical finite difference scheme on the IBM 7090 computer.

The boundary conditions on the pressure are given by the aerodynamic pressure acting on the surface

$$p_w = p(t) \quad (10)$$

and by a zero pressure gradient at the backface.

$$\frac{\partial p}{\partial x} = 0 \quad (11)$$

The boundary conditions on the temperature are given by the condition of no heat transfer at the backface

$$\frac{\partial T}{\partial x} = 0 \quad (12)$$

and by the net heat flux at the surface

$$q_{NET}(t) = -k \frac{\partial T}{\partial x} \quad (13)$$

Various expressions for the net heat flux have been used in similar investigations (Ref. 8, 10, 18). In the present analysis, the net heat flux to the surface is taken to be (Ref. 18)

$$q(t)_{NET} = q(t)_{CONVECTIVE} + q(t)_{HOT\ GAS\ RADIATION} - q(t)_{RERADIATION} - q(t)_{BLOCKING} \quad (14)$$

Before the char is formed, the surface temperature is still relatively low and the net heat flux is the convective heat flux. As char is formed, gaseous products are also formed and they flow out through the front surface of the char and block an appreciable amount of the convective heat flux. As the surface temperature becomes higher, re-radiation of a portion of the heat back into the environment may contribute significantly to reducing the net heat flux to the surface. Also, the hot gas radiation to the surface is included.

Initial conditions for the temperature and gas pressure must also be prescribed.

#### D. RESULTS

Results are presented for a re-entry body subjected to transient environmental conditions which are typical of the early portion of a re-entry trajectory - Figure 1. The material and gas properties used in the calculations are given in Tables I and II. Both the environmental conditions and properties were chosen for illustrative purposes.

The results for a material which undergoes one degradation reaction are presented in Figures 2-6. The lower heat flux curve in Figure 1 was used for these calculations. The distributions of temperature, material density, and gas pressure through the heat protective layer are presented as a function of time. The mass flux of the gases at the surface is also given.

The mass flux of gases (Figure 4) is relatively small. Therefore, the blocking effect on the net heat flux is not significant. The surface temperature increases and the general shape of the temperature distribution curve does not change (Figure 2).

The continuous variation of the material density is presented in Figure 3. The final char is formed at the surface after a period of thirteen seconds.

One of the most significant results is that of the variation in gas pressure from the surface through the porous material to the original non-porous material (Figure 5). This illustrates the build up of gas pressure within the material. The permeability affects this pressure variation (Figure 6). The gases flow more easily as the permeability is increased, therefore, the pressure does not build up as rapidly and the gas pressure is distributed more evenly through the material.

Similar results are presented in Figures 7-10 for a material which undergoes two reactions as the material degrades. The upper heat flux in Figure 1 was used for these calculations.

The mass flux of gases (Figure 10) is considerably higher for this case. The surface temperature increases for the first fifteen seconds. Then it decreases due to the blocking action effect. In fact,

the temperature through the char layer decreases while the temperature through the first reaction zone and original plastic material remains essentially the same.

The material density variation is given in Figure 8. A definite char thickness of approximately .012 in. is formed after 16 seconds. The shape of the curve changes because of the two reactions which occur.

The gas pressure within the material (Figure 9) increases more rapidly because of the two reactions. The results presented for both cases are characteristic of the initial transient response of many charring ablators.

#### **E. CONCLUDING REMARKS**

The results demonstrate that the analysis presented in this report is capable of providing detailed calculations of the transient behavior of charring ablators. The continuous variation of the temperature, gas pressure, and material density through the heat protective layer are calculated as a function of time. The mass flux at the surface is also calculated. From this, the total material ablated can be calculated and the amount of protective heat shield necessary for a given design condition estimated.

It should be pointed out that the accuracy of the calculations depends upon the degree of certainty with which the mechanical, chemical, and thermodynamic properties of the materials and gases are known. The results are very sensitive to the frequency factor and activation. Therefore, these quantities should be determined quite accurately for the materials of importance. Also, the gas pressure build-up within the material depends very strongly upon the permeability. The permeability is a complicated function of many quantities. It is necessary to determine the important quantities and the functional dependence of the permeability on these quantities.

Calculations of the char removal were not performed. The basic mechanisms (such as, surface oxidation and mechanical stresses) can be included as a modification to the heat flux boundary condition or as an additional calculation. The char removal can also be calculated by assuming that the char thickness remains constant. The char surface then recedes at the same rate as the reaction zone. It is also possible to specify other rates of surface recession, depending upon the material. Thus, the analysis is applicable to a wide range of materials which undergo thermal degradation in depth.

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## NOMENCLATURE

### SYMBOLS

$a$	Exponent in Eq. (8)
$A$	Frequency Factor
$b$	Exponent in Eq. (9)
$C_p$	Specific Heat
$E$	Activation Energy
$f$	Porosity
$H_c$	Heat of Cracking
$H_R$	Heat of Degradation Process
$k$	Thermal Conductivity
$K$	Permeability
$\dot{m}$	Mass Flux
$\bar{M}$	Mean Molecular Weight
$n$	Exponent in Eq. (5)
$p$	Pressure
$q$	Heat Flux
$R$	Gas Constant
$t$	Time
$T$	Temperature
$u$	Velocity
$\dot{w}_g$	Rate of Formation of Gases
$\dot{w}_p$	Rate of Plastic Degradation
$x$	Distance Normal to Surface
$\rho$	Density
$\Gamma$	Gasification Ratio

**NOMENCLATURE (Cont'd)**

**SUBSCRIPTS**

c	Char Material
g	Gases
V. P.	Original Plastic Material
w	Surface

TABLE I - CONSTANT PROPERTY DATA

DENSITY: lb./cu. ft.

Virgin Plastic, v.p. 75

Primary Char, p.c. 45

Secondary Char, s.c. 10

PERMEABILITY:  $K_c, \frac{\text{Ft.}^4}{\text{lb. sec.}}$   $.18 \times 10^{-4}$

POROSITY,  $f_c$  .9

GASIFICATION RATIO,  $\Gamma$  .7

FREQUENCY FACTOR: 1/sec

$A_1$   $1.0 \times 10^5$

$A_2$   $2.8 \times 10^5$

ACTIVATION ENERGY:  $\frac{\text{KCAL}}{\text{Mole}}$

$E_1$   $36 \times 10^3$

$E_2$   $50 \times 10^3$

HEAT OF PYROLYSIS:  $\frac{\text{BTU}}{\text{lb.}}$

$Hr_1$  100

$Hr_2$  500

TABLE II - VARIABLE PROPERTY DATA

MATERIAL PROPERTIES

<u>TEMPERATURE</u>	<u>SPECIFIC HEAT</u>	<u>THERMAL CONDUCTIVITY</u>
T, °R	$\frac{\text{BTU}}{\text{lb. °R}}$ $C_{p_s}$	$\frac{\text{BTU}}{\text{Ft. Sec. °R}}$ $k_s$
600	.403	$.284 \times 10^{-4}$
860	.423	$.382 \times 10^{-4}$
1250	.435	$2.0 \times 10^{-4}$
1650	.440	$7.5 \times 10^{-4}$
2000	.450	$10.8 \times 10^{-4}$
2500	.467	$15.4 \times 10^{-4}$
3000	.483	$24 \times 10^{-4}$
3500	.500	$24 \times 10^{-4}$

PROPERTIES OF GASEOUS PRODUCTS:

<u>TEMPERATURE</u>	<u>SPECIFIC HEAT</u>	<u>THERMAL CONDUCTIVITY</u>	<u>HEAT OF CRACKING</u>	<u>MOLECULAR WEIGHT</u>
°R	$\frac{\text{BTU}}{\text{lb. °R}}$ $C_{p_g}$	$\frac{\text{BTU}}{\text{Ft. Sec. °R}}$ $k_g$	$\frac{\text{BTU}}{\text{lb. °R}}$ $H_c$	$\bar{M}$
600	.24	$3 \times 10^{-6}$	0	72
860	.26		0	72
1250	.54	$7 \times 10^{-6}$	0	66
1650	.75		$.1 \times 10^{-1}$	55
2000	.83		$.5 \times 10^{-1}$	50
2500	.92		$.75 \times 10^{-1}$	20
3000	1.00	$20 \times 10^{-6}$	$1. \times 10^{-1}$	20
3500	1.00		$1.6 \times 10^{-1}$	10

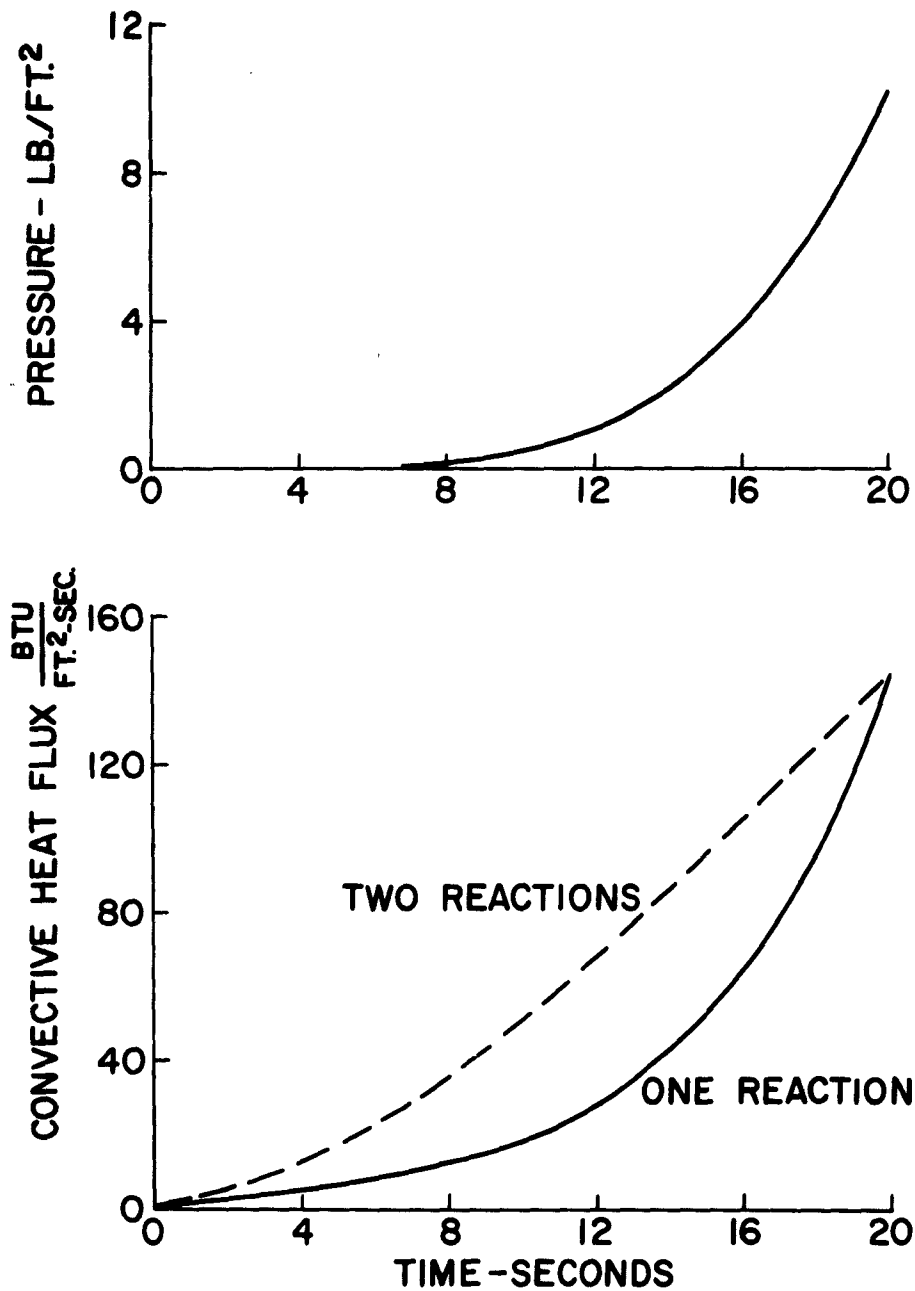


Figure 1. Environmental Conditions

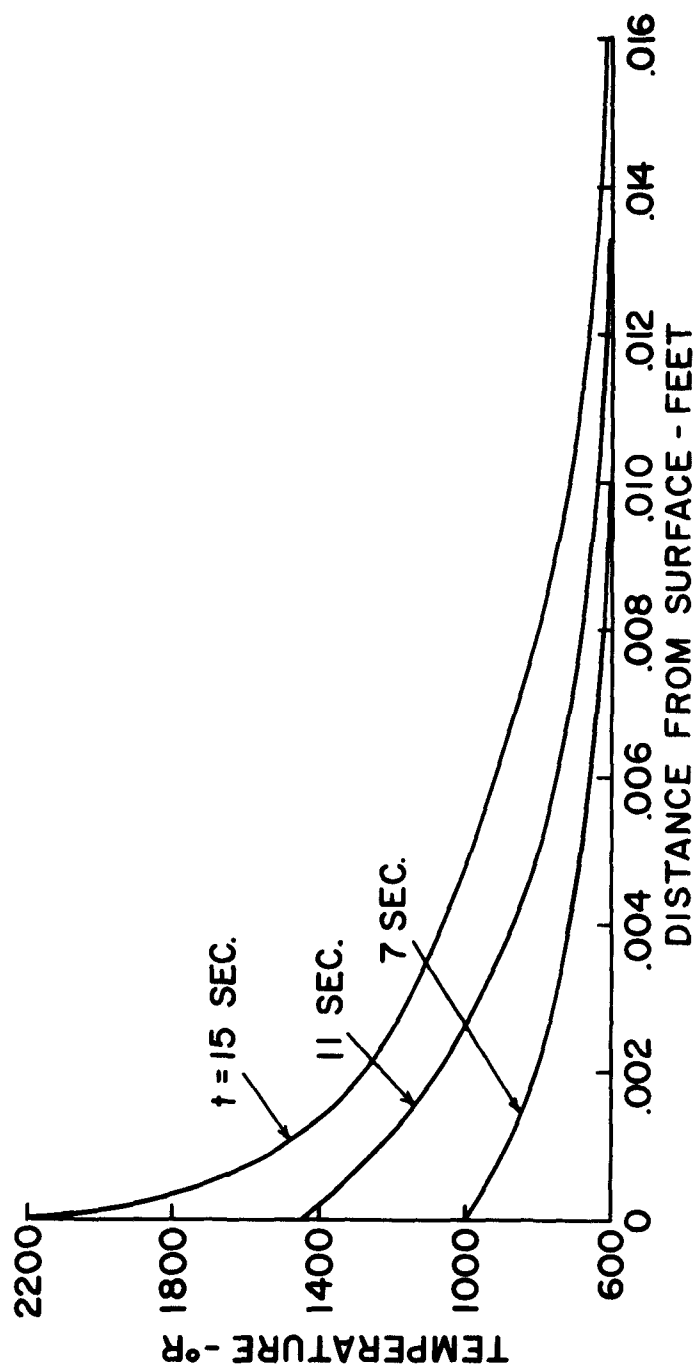


Figure 2. Temperature Distribution (One Reaction)

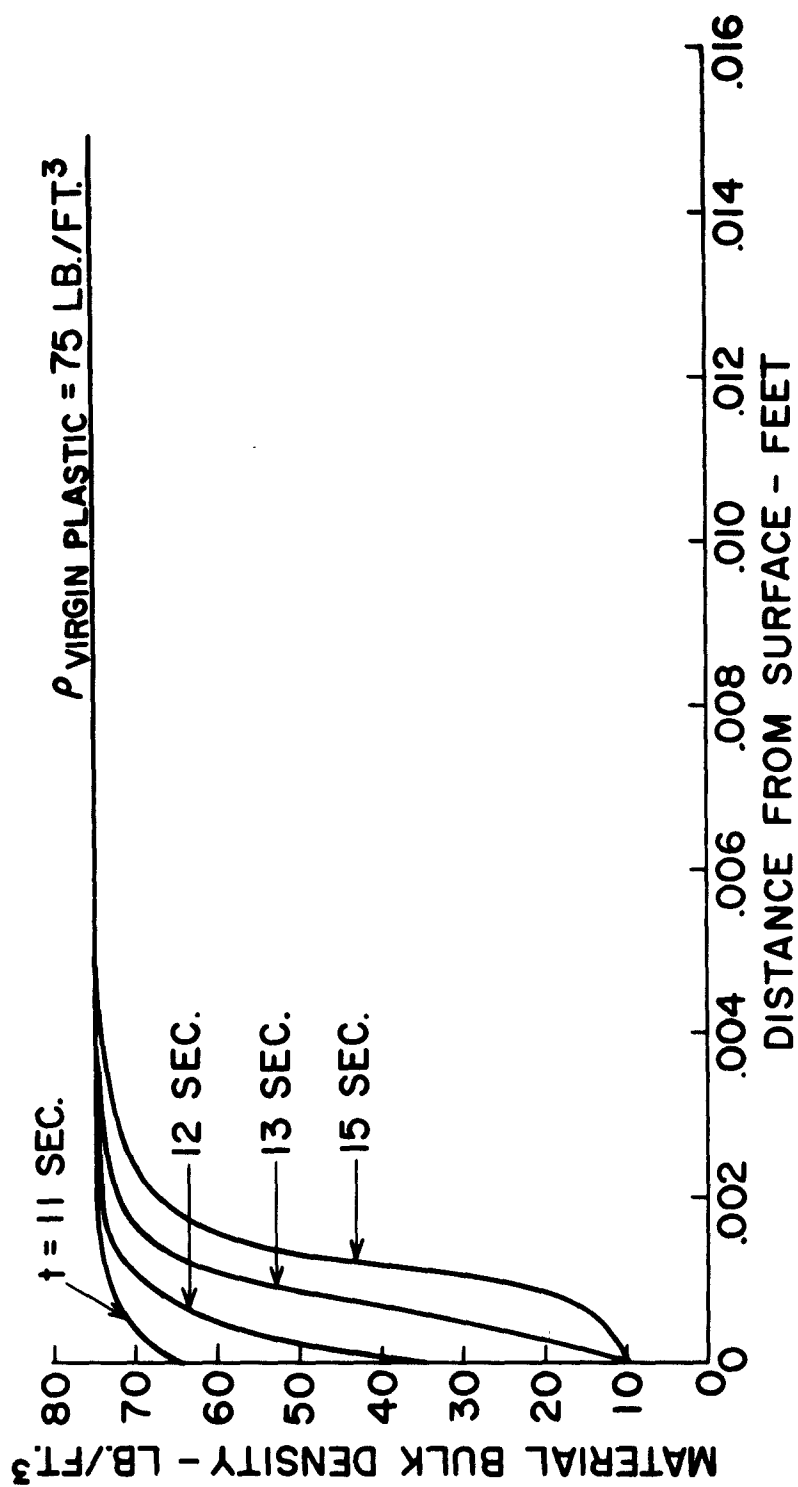


Figure 3. Material Density Variation (One Relation)

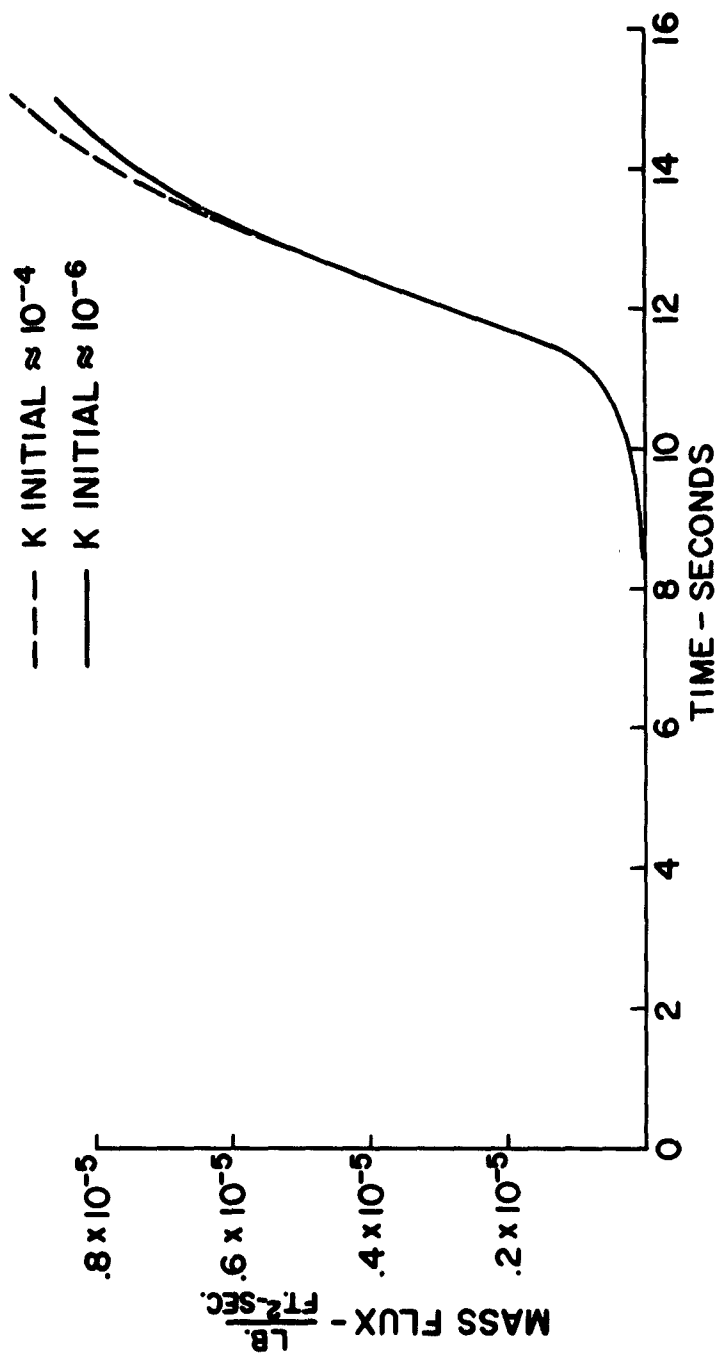


Figure 4. Mass Flux at Surface (One Reaction)

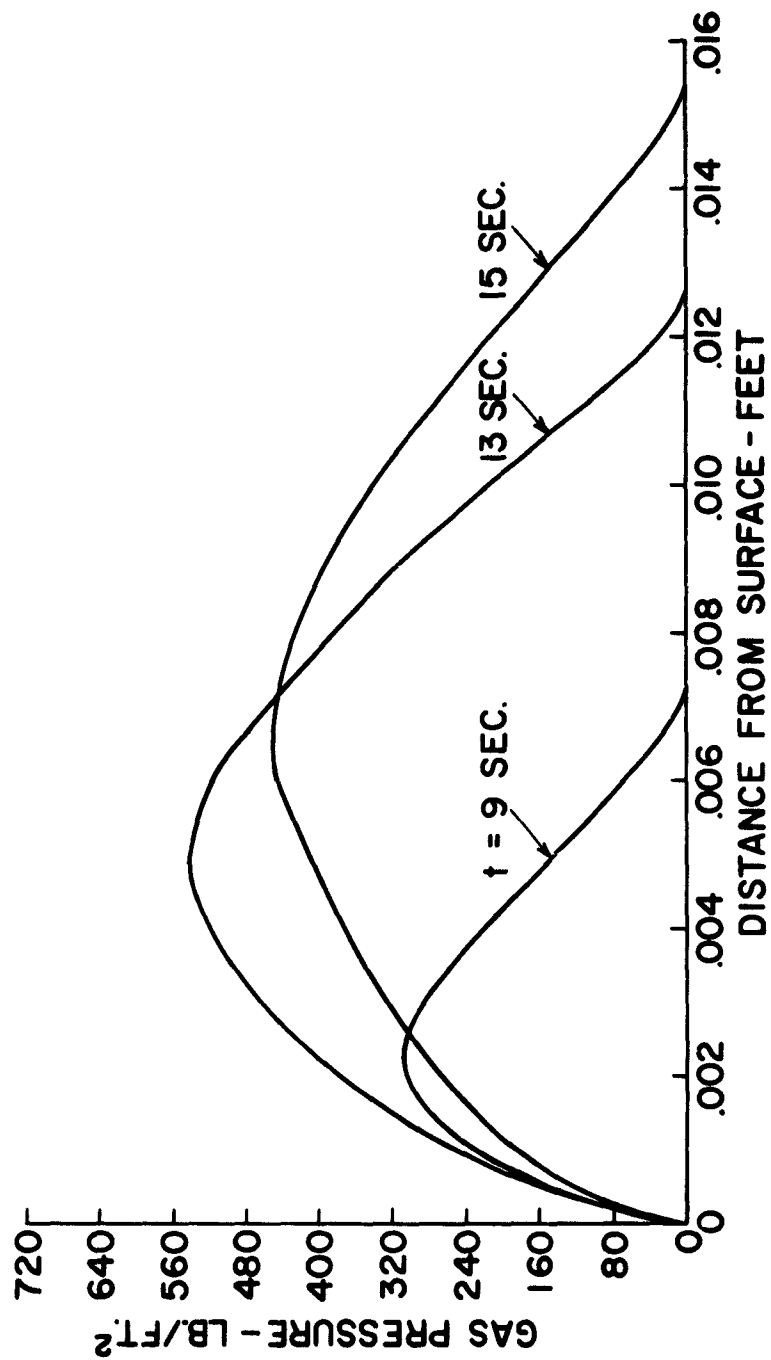


Figure 5. Gas Pressure (One Reaction)

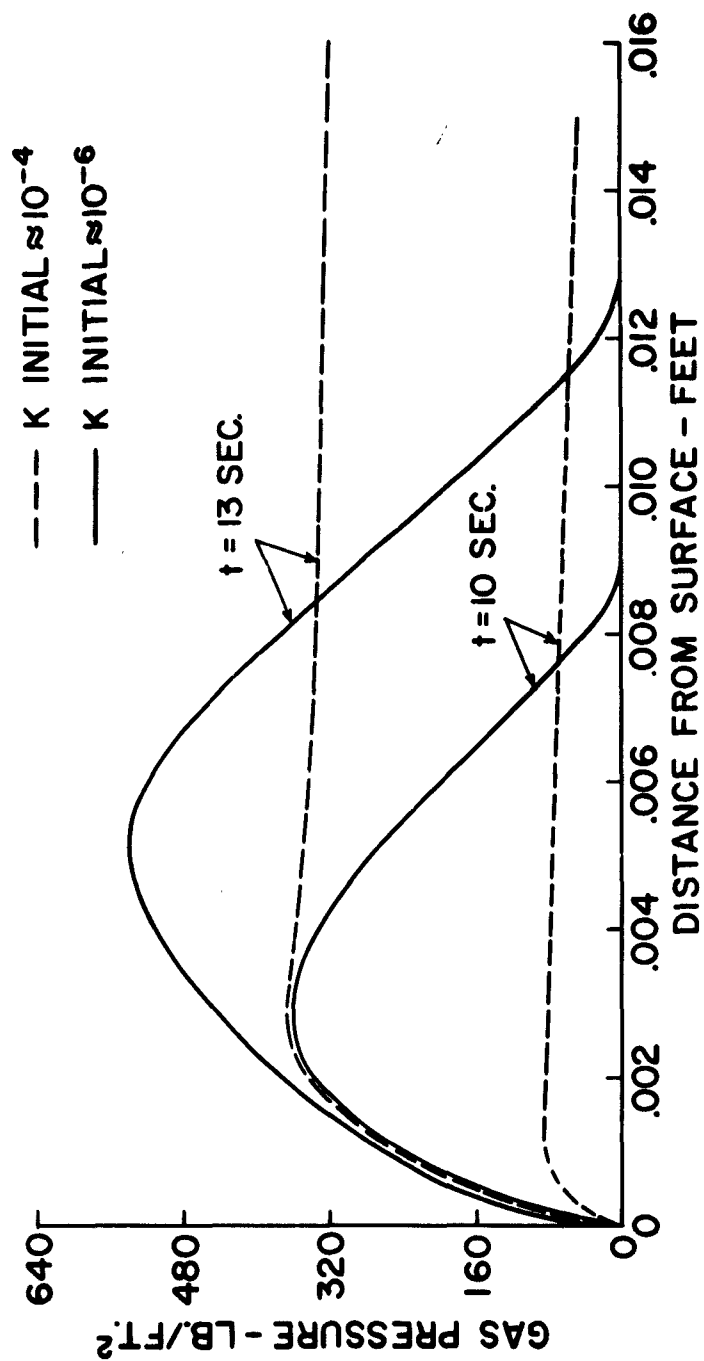


Figure 6. Effect of Permeability Factor

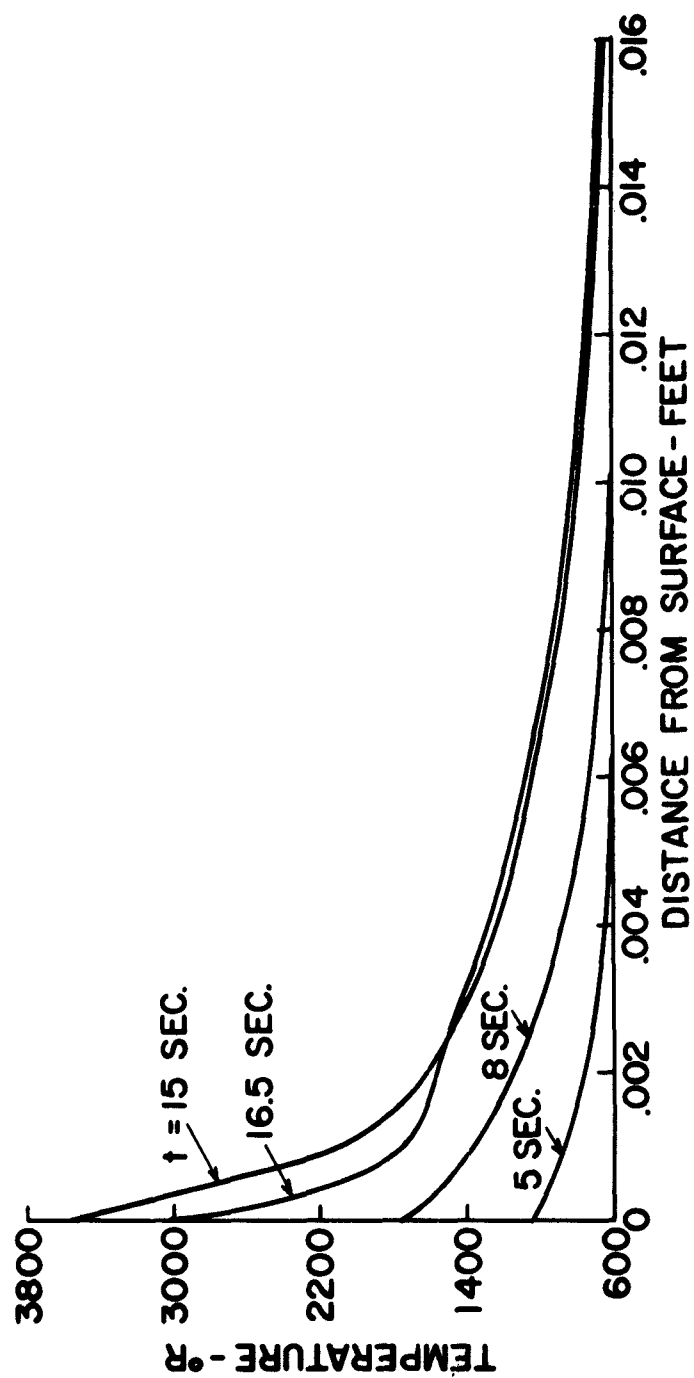


Figure 7. Temperature Distribution (Two Reactions)

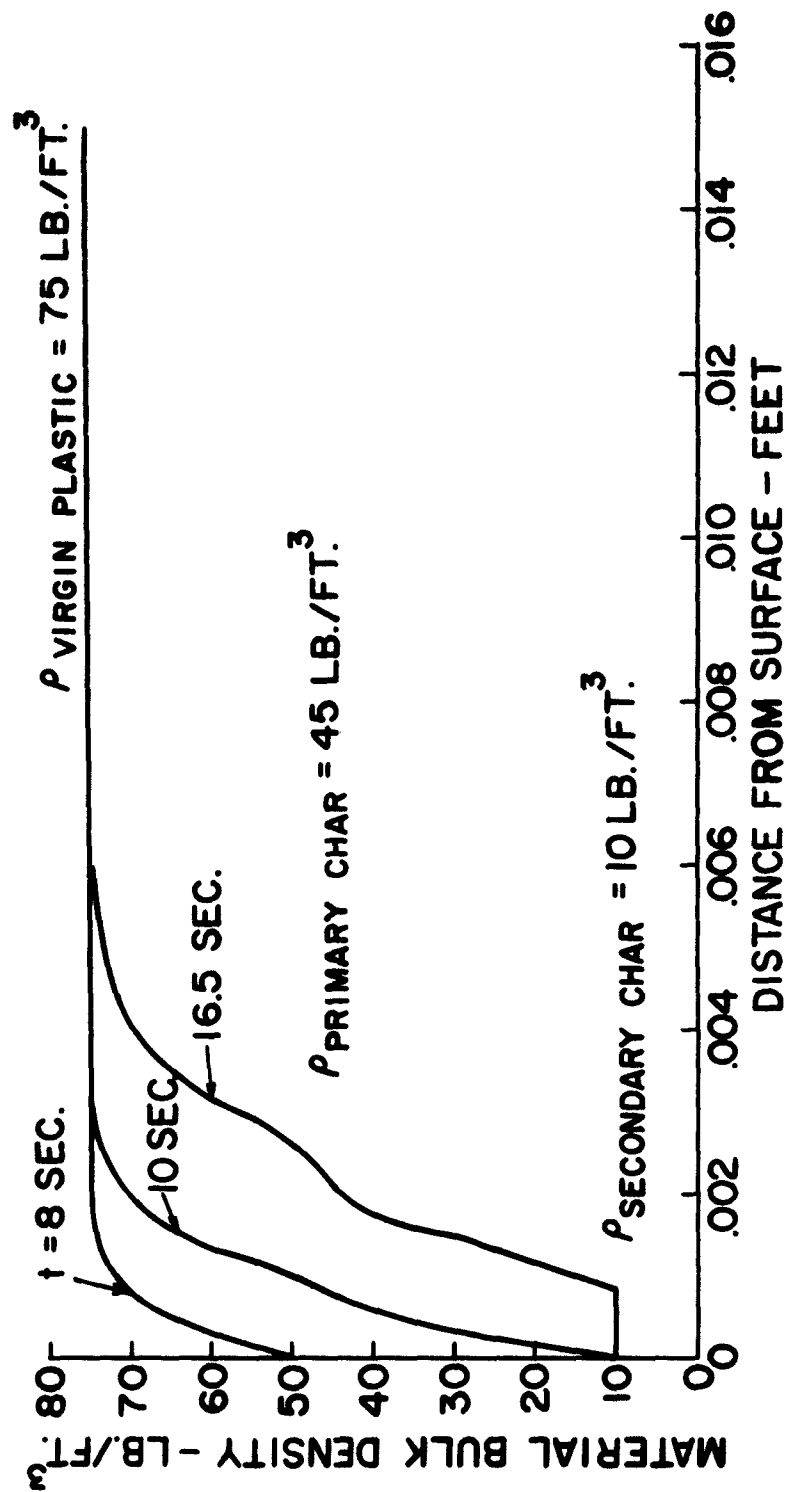


Figure 8. Material Density Variation (Two Reactions)

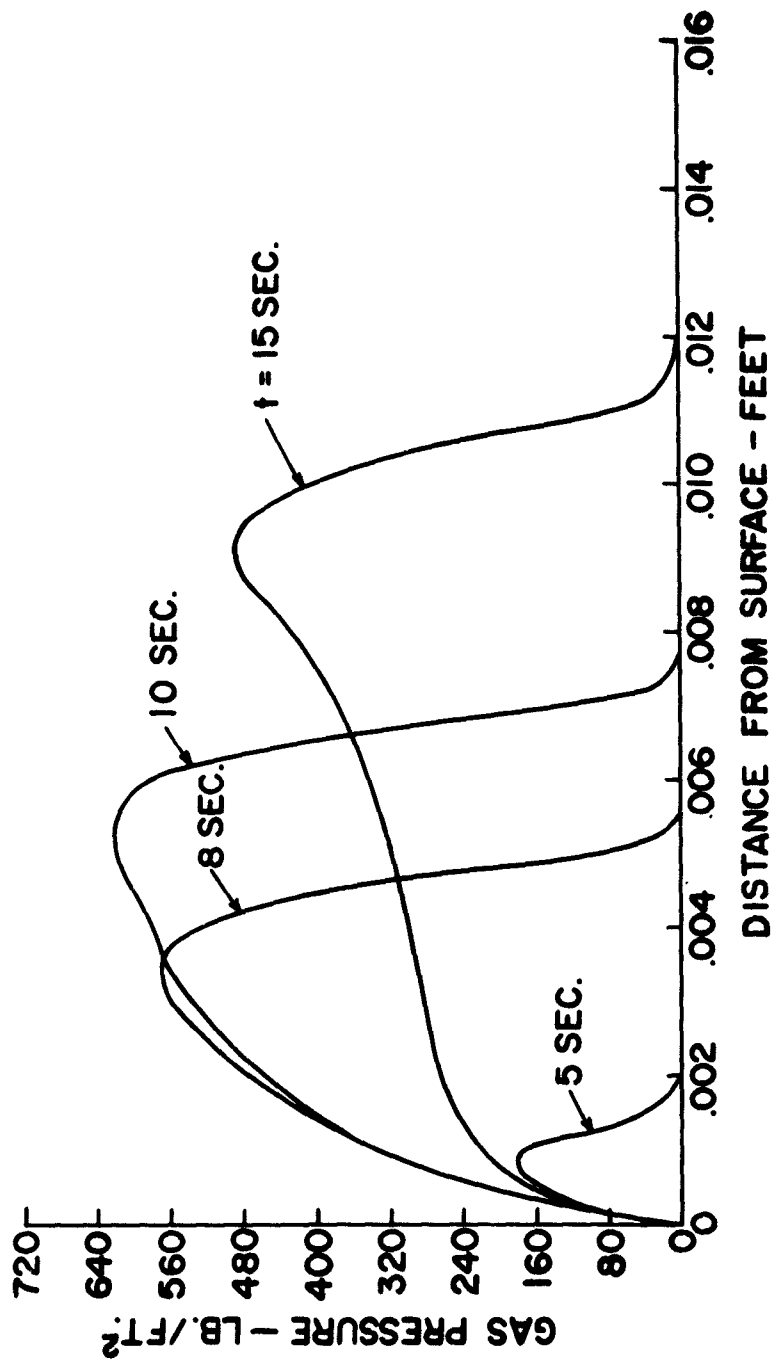


Figure 9. Gas Pressure (Two Reactions)

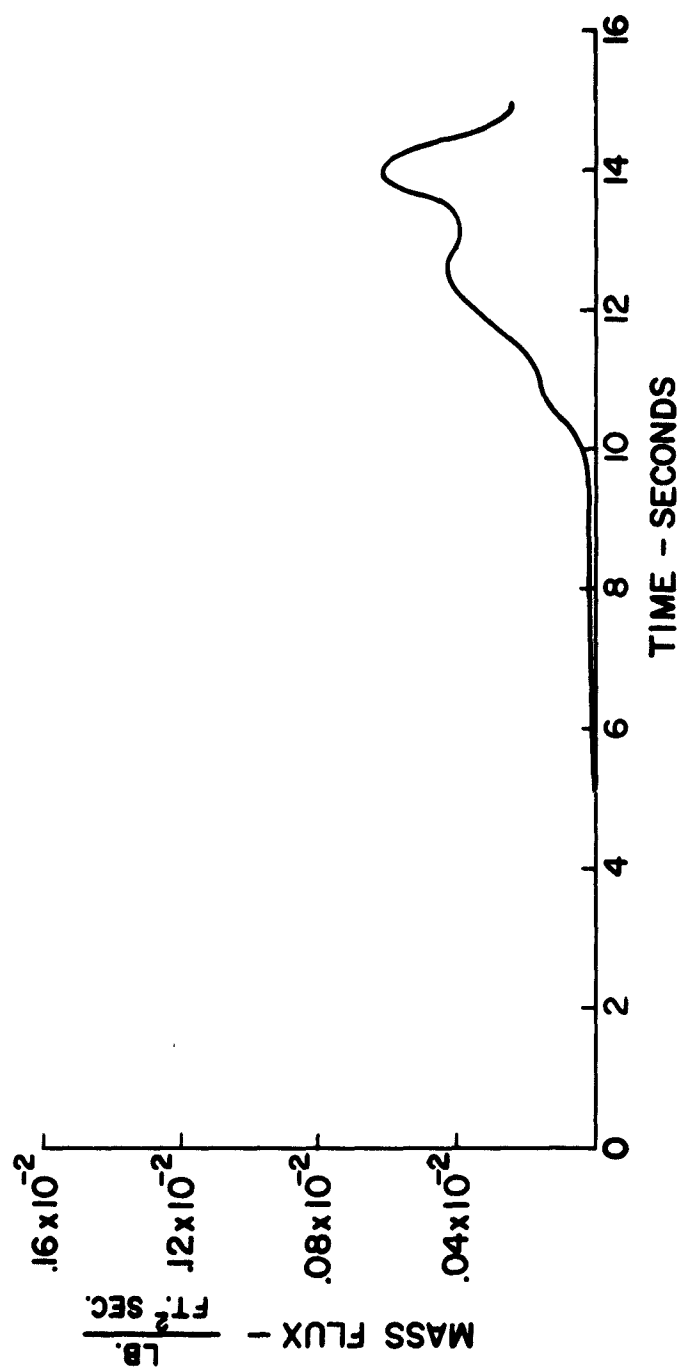


Figure 10. Mass Flux at Surface (Two Reactions)



SPACE SCIENCES LABORATORY  
MISSILE AND SPACE DIVISION

### TECHNICAL INFORMATION SERIES

AUTHOR	SUBJECT CLASSIFICATION	NO.
R. Mathieu	Hyperthermal Environment	R63SD20
		DATE
		Feb. 1963
TITLE		S. S. CLASS
RESPONSE OF CHARRING ABLATORS TO HYPERTHERMAL ENVIRONMENT		I
		GOV. CLASS
		None
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		36
SUMMARY		
<p>A study is made of the thermal response of charring ablators to given environmental conditions. The heat protective materials considered form gases and a porous char as they undergo thermal degradation in depth. The analysis considers the transient conditions and the effect of the surface pressure on the gas pressure build-up within the porous char. The effects of porosity and permeability are included.</p> <p>Results of the temperature, material density, and gas pressure distribution through the heat protective layer are presented for a typical charring material. Two cases are considered: in the first case, the material undergoes one degradation reaction; in the second case, the material undergoes two successive reactions.</p> <p>The inclusion of char removal can also be accomplished by this study.</p>		

By cutting out this rectangle and folding on the center line, the above information can be fitted into a standard card file.

AUTHOR

*R. D. Mathieu*

COUNTERSIGNED

*H. G. Lent*

*John F. Fisher*